Oxidative Dehydrogenation of Ethane to Ethylene in an Oxygen Ion Transport Membrane Reactor – A Model for Process Intensification

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The vast majority of ethylene produced in the world is made by steam cracking of ethane – a process characterized by high temperatures and very short residence times. The production of ethylene in steam cracking is, however, equilibrium-limited; and the typical single pass conversion of ethane at 827 °C is 75.6% with a selectivity to ethylene of only 78.3% [1]. As a result, the backend separation train is both Capex and Opex intensive.

It is possible to oxidatively dehydrogenate ethane to ethylene with higher yields and selectivities; but this process requires an air separation unit (ASU) to produce pure oxygen and has safety risks associated with mixing oxygen and hydrocarbons at elevated temperatures.

An eloquent solution to the problem is the use of an oxygen ion transport (ITM) membrane reactor wherein the oxygen is supplied from air or from water splitting on the upstream side of the membrane and is provided on an as-needed basis for oxidative dehydrogenation of ethane on the downstream side of the membrane. As a result, there is no expensive ASU required; and safety concerns are significantly reduced.

In this study, we used a mixed ionic electronic conducting (MIEC) membrane made from $BaFe_{0.9}Zr_{0.1}O_{3-\delta}$ mounted in a button cell reactor to split water on the upstream side of the membrane (Reaction [1] below). Oxygen ions produced in this process diffused through the membrane and reacted with ethane on the downstream side to produce ethylene and water (Reaction [2] below).

$$H_2O + 2e^- \rightarrow O^= + H_2 \quad [1]$$

$$C_2H_6 + O^= \rightarrow C_2H_4 + H_2O + 2e^- \quad [2]$$

At 900 °C and 10% C_2H_6 in argon as the feed, an oxygen flux (J_{O2}) of ~ 2.0 μmole/cm²/sec was observed, while the ethane conversion and selectivity to ethylene were 95% and 83%, respectively. Thermal gas phase reactions at 900 °C resulted in the formation of undesired products and a lower ethylene selectivity. Reduction of the temperature to 850 °C decreased the oxygen flux to ~1.0 μmole/cm²/sec and conversion of ethane to 79% (still higher than steam cracking). Interestingly, the ethylene selectivity increased to 93% (a significant improvement over steam cracking). This large increase in selectivity along with the elimination of the need to separate hydrogen from hydrocarbons in the product stream can lead to a substantial decrease in capital and operating costs for the membrane reactor system.

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[1] Van Goethem, M.W.M. et al., ***Chem. Eng. Res. Des. 91*** 2013 1106-1110.